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HARDENED SOLAR ARRAY HIGH TEMPERATURE ADHESIVE

C. Beard
C. Sherwood
D. Basiulis
P. Magallanes
G. Wolff
H. Levin

HUGHES AIRCRAFT COMPANY
Space and Communications Group
P.O. Box 92919 Airport Station
Los Angeles, CA 90009

APRIL 1981

TECHNICAL REPORT for
Period April 1980 - January 1981

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This technical report has been reviewed and is approved for publication.

Kenneth T. Masloski

KENNETH T. MASLOSKI, 2Lt, USAF
Project Engineer
Energy Conversion Branch

Joseph Wise

JOSEPH F. WISE
TAM, Solar/Thermal Power
Energy Conversion Branch
Aerospace Power Division

FOR THE COMMANDER

Reams

JAMES D. REAMS
Chief, Aerospace Power Division
Aero Propulsion Laboratory

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resulted from careful and orderly experimentation involving the main elements of the problem, namely, (a) purification of reactants and solvents, (b) preparation, workup, and characterization of monomers, (c) preparation and workup of prepolymers, (d) development of a trace level, silanol end group analysis for estimating prepolymer advanceability, and (e) prepolymer advancement to the final polymer. Significant additional progress in the prepolymer preparation and advancement steps is still required for definition of a reproducible process for preparing the ultrahigh molecular weight material. Pending achievement of such progress, adhesive formulation efforts are limited.

FOREWORD

This final report, "Hardened Solar Array High Temperature Adhesive" covering the period from April 1980 to January 1981, was prepared by Hughes Aircraft Company Space and Communications Group, El Segundo, California under Contract F33615-80-C-2015. The work was administered under the direction of J.E. Beam and Lt. K. Masloski, POOC-2, Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories. Contributors include Dr. M.F. Hawthorne of the University of California, Los Angeles; Dr. R.W. Lenz and Dr. Yu-Chin Lai of the University of Massachusetts; Dr. E. Hedaya of Union Carbide Corporation; and Dr. C.D. Beard, Dr. C.H. Sherwood, D.I. Basiulis, P.G. Magallanes, G. Wolff, and H. Levin of Hughes Aircraft Company. This report was submitted by the authors 23 January 1981.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

Previous work[1] at Hughes (supported by the Air Force Aero Propulsion Laboratory) indicated the attractiveness of ultrahigh molecular weight D_2-m-carborane-siloxane linear polymers for use as high temperature, thermoplastic adhesives in bonding solar cell arrays to substrates. Evaluation testing was constrained by the small amount of experimental material (UCARSIL) available at that time from the supplier, Union Carbide Corporation (UCC). Subsequent efforts by UCC to supply additional ultrahigh molecular weight material proved unsuccessful.

This report reviews the work attempting to develop a reproducible process for preparing these ultrahigh molecular weight polymers. This work was conducted under Air Force contract F33615-80-C-2015, Hardened Solar Array High Temperature Adhesive. The work of the program was divided into three phases as follows:

Phase I - Initial Investigation. Develop a reproducible synthesis for pertinent polymeric materials required and characterize same.

Phase II - Adhesive Formulation. Blending of materials and preparation of film adhesive therefrom. Characterization of film adhesive.

Phase III - Adhesive Testing. Investigate adhesive processing behavior with various pertinent coupon materials. Prepare test coupons and perform tests.

Section II of this report describes the progress made in Phase I of the program. While real progress has been made in this phase, the objective of developing a reproducible preparation process for these polymers has not been met in the allotted eight month funded experimental portion of the program. This fact has prevented any significant effort being devoted to Phases II and III.

Hughes Aircraft feels that, given the substantial progress already made and the incentive of ongoing system hardening requirements, additional funding is well justified for this effort to produce a breakthrough in high temperature stable elastomeric adhesives.

SECTION II

INITIAL INVESTIGATION

This initial task was designed to develop a reproducible process for preparing ultrahigh molecular weight m-carborane-siloxane polymers with improved characterization over that previously available. It is believed that such additional processing and characterization detail, while undoubtedly required in developing the synthesis, would be of considerable benefit in the subsequent formulation of film adhesives from the synthesized polymers.

1. DEVELOPMENT OF A REPRODUCIBLE SYNTHESIS OF ULTRAHIGH MOLECULAR WEIGHT CARBORANE-SILOXANE POLYMER

a. Statement of the Problem

In general, carborane-siloxane polymers routinely synthesized using the UCC method ($\overline{M}w \sim 140,000$, RV ~0.5) were considered satisfactory for the majority of the anticipated end use applications. However, higher molecular weight theoretically would give higher performance materials with improved physical properties for very demanding aerospace applications. For example, a significant improvement in properties with increasing molecular weight up to $\overline{M}w \simeq 500,000$ was observed for polydimethylsiloxane.[2]

Accordingly, ultrahigh molecular weight carborane-siloxane polymers ($\overline{M}w > 10^6$, RV ≥3) were subsequently prepared at UCC by a two-step procedure in which a silanol terminated prepolymer ($\overline{M}w \sim 140,000$, RV ~0.5) was isolated after a hydrolytic workup, purified, and then titrated with additional bisureidosilane resulting in a molecular weight advancement to $>10^6$. The ultrahigh molecular weight polymers exhibited large improvements in tensile strength and elongation, and vastly superior thermal stability in air up to 800°C.[3] This improvement in properties was attributed to increased chain entanglement.

Unfortunately, subsequent experiments almost a year later at UCC did not give reproducible ultrahigh molecular weight polymer. The reasons for this failure have not yet been defined. The UCC two-step procedure as of July, 1978 is presented in Figure 1 and marks the conclusion of the UCC work in this field and also is the basis for the Hughes effort described herein.

Little or no precedent exists for the construction of high polymers by a two-step process as described in Figure 1; thus, it is not surprising that

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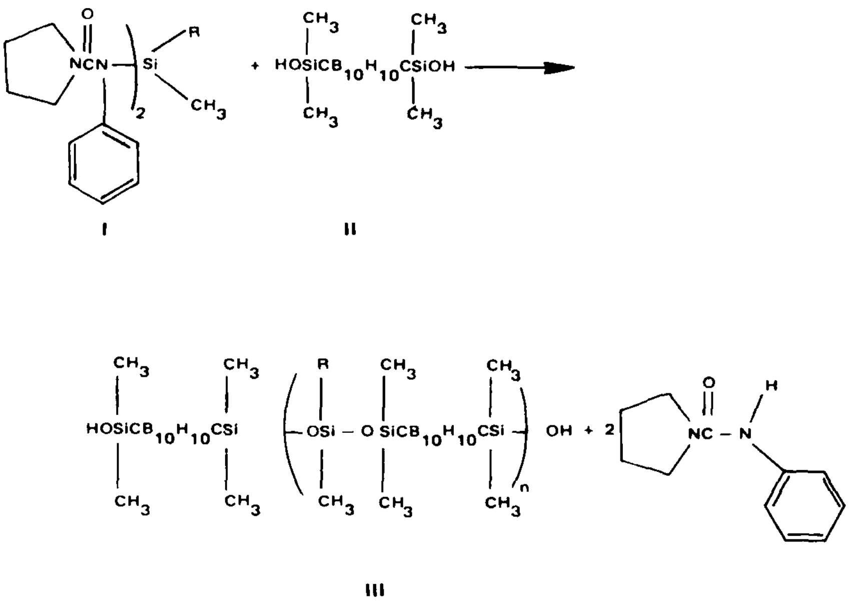
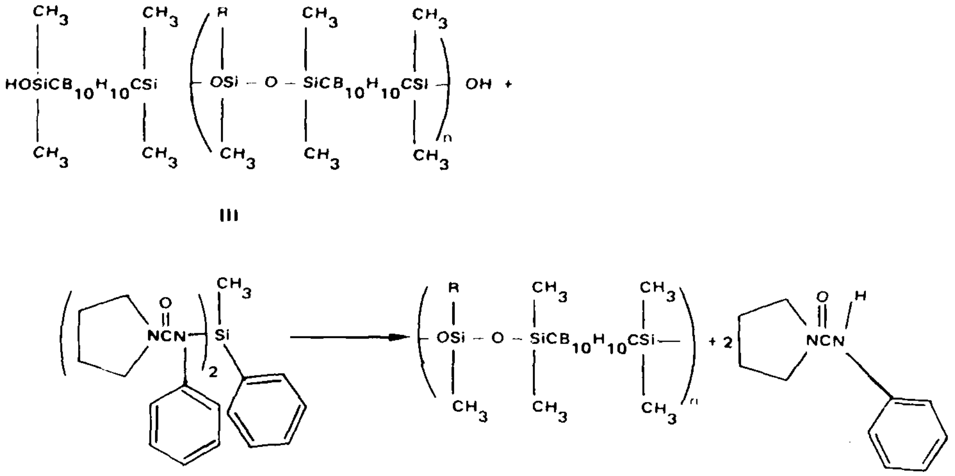


a. CARBORANE SILANOL TERMINATED CARBORANE SILOXANE PREPOLYMER

A 250-ml, three-neck flask was equipped with a mechanical stirrer, a nitrogen inlet, and a 100-ml, one-neck satellite flask. Carborane disilanol (28.3 gram, 0.097 mole) was weighed into the 250-ml flask. Bis(ureido)methylphenylsilane (14.3 gram, 0.029 mole) and bis(ureido)dimethylsilane (25.1 gram, 0.057 mole) were weighed into the 100-ml satellite flask under nitrogen. The flask containing the mixed bis(ureido)silanes was connected to the 250-ml flask with a flexible solids addition tube. Dried chlorobenzene (28 ml) was added to the carborane disilanol and the slurry was stirred and cooled to -10 ±5°C. A portion-wise addition of the solid bis(ureido)silanes was conducted over 4 hours. At the conclusion of the addition period, 1 ml of chlorobenzene was syringed into the reaction flask to wash the remaining solids into the reaction mass. The reaction was cooled for an additional 1.5 hour at -10 ±5°C, followed by additional cooling of the reaction flask in an ice bath. The reaction was then allowed to warm up to ambient temperature overnight. The carborane siloxane reaction mass was diluted with chlorobenzene and filtered to remove the solid reaction byproduct. The carborane siloxane/chlorobenzene solution was precipitated three times from a large volume of methanol or acetonitrile. The precipitated polymer was then vacuum pumped to remove retained solvents. The recovered polymer weighed 27.2 gram (85.6 percent), reduced viscosity (RV) = 0.53 dl/gm in $CHCl_3$ at 25°C.

FIGURE 1. UNION CARBIDE TWO-STEP SYNTHESIS OF ULTRAHIGH MOLECULAR WEIGHT CARBORANE-SILOXANE POLYMERS.[3]



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b. ULTRA-HIGH MOLECULAR WEIGHT D_2–m-CARBORANE SILOXANE.

A 100-ml, one-neck flask was equipped with a magnetic stirring bar and a nitrogen inlet. Carborane siloxane polymer (5.0 gram, 1.1×10^{-4} mole) was weighed into the flask, and the flask was vacuum pumped at 100°C overnight to dry the sample. The flask was septum sealed under nitrogen and cooled; 25 ml of dry chlorobenzene was added by syringe. The flask was shaken to dissolve the polymer prior to being placed over a magnetic stirrer. The polymer solution was slowly stirred under a nitrogen blanket. Bis(ureido)methylphenylsilane (0.19 gram, 3.77×10^{-4} mole) in 2.0 ml of dry chlorobenzene was slowly titrated into the polymer solution until the polymer solution became extremely viscous. The polymer mass was then back titrated with carborane disilanol (0.04 gram, 1.4×10^{-4} mole) in 20 ml of chlorobenzene over 5.0 hours. The carborane siloxane polymer was diluted with 30 ml of chlorobenzene and poured into 500 ml of methylene chloride to lower the viscosity of the polymer solution. The polymer was precipitated from 3 liters of methanol and vacuum dried at 100°C. The recovered ultrahigh molecular weight polymer weighed 4.7 gram (94.0 percent), RV = 5.12 dL/gm in $CHCl_3$ at 25°C.

FIGURE 1. (continued) UNION CARBIDE TWO-STEP SYNTHESIS OF ULTRAHIGH MOLECULAR WEIGHT CARBORANE-SILOXANE POLYMERS.[3]

reproducibility problems have arisen in the development of this pioneering approach. Traditionally, however, three factors generally are recognized as most important for a successful step growth polymerization (i.e., prepolymer preparation, Figure 1) as follows:

- Minimum Competing Side Reactions. In the present system side reactions are probably not serious since high molecular weight can be obtained routinely. [Often side reactions (e.g., cyclization) occur relatively early in the polymer chain buildup and are not serious thereafter (statistically, the formation of large rings is unlikely).]

- An Exact Equivalence of Functional Groups. A 6 percent stoichiometric excess of $\underline{m}$-$C_2B_{10}H_{10}(SiMe_2OH)_2$ was used (Figure 1), but apparently the stoichiometry requirement for high polymer construction was satisfied by the heterophase reaction conditions which permitted the relatively insoluble disilanol to be slowly transferred into the solution phase and "titrate" ureidosilane terminated oligomer. In theory, a 6 percent excess of disilanol should have given a prepolymer with $\overline{M}_w$ ~20,000 instead of the 140,000 actually obtained.

- High Monomer Purity. It is axiomatic in polymer chemistry that erratic results and a limit to the degree of polymerization can be attributed to impurities in the monomers, and this has been suggested by many as the most likely source of problems in the case of ultrahigh molecular weight polymers. We reject this hypothesis for two reasons: first, the prepolymer molecular weight obtained is essentially constant and not what would be expected for variable amounts of monomer impurity; and second, the monomer melting temperature ranges do not vary from batch to batch and are, in our opinion, very sensitive to purity variations.

To summarize, the lack of a reproducible process cannot readily be attributed to any of the traditional step growth factors. However, in the UCC synthesis a silanol terminated prepolymer is actually isolated and purified, thereby, introducing numerous additional experimental uncertainties. Thus, the process can be divided into three distinct areas for experimental evaluation as shown below: A great deal must be learned about each area in order to establish a reproducible synthesis of ultrahigh molecular weight polymer. Our strategy for accomplishing this goal is discussed in section II, paragraph 1.b.

- Prepolymer preparation

- Prepolymer workup, isolation, and purification

- Molecular weight advancement

b. Hughes Research Strategy

At the beginning of this program the major question was "Is the lack of reproducibility caused by (1) batch to batch variation in prepolymer silanol content or (2) are silanol groups always present in the prepolymer and the advancement reaction quenched sometimes by unknown impurities?" The overwhelming consensus was that the advancement reaction was probably reliable and that silanol content was in some way determined by minor technique variations during the hydrolytic workup and purification of the prepolymer. The two opposing points of view were that Si-OH was destroyed by excessive heating during drying or alternatively that Si-OH was generated during the workup, presumably by hydrolysis of an unknown SiX end group. A parametric investigation of the prepolymer workup and isolation procedure was therefore strongly indicated.

Thus, experimental work was initiated and since our experience with the polymerization experiments was not extensive we chose initially to repeat the UCC work as follows:

- Synthesize monomers (section II, paragraph 1.c).
- Repeat UCC prepolymer preparation (section II, paragraph 1.e).
- Carry out prepolymer advancement using samples provided by UCC, portions of which had previously been advanced (section II, paragraph 1.f).

Both monomer synthesis and prepolymer preparation proceeded smoothly, however, the advancement reaction was unsuccessful (section II, paragraph 1.f).

It was now apparent that batch variations in silanol content as well as erratic advancement reactions, even though silanol content had been demonstrated, could be anticipated. In retrospect, it was fortunate that we learned early in the program that the ability to undergo the advancement reaction was not a reliable criterion of silanol content. This, of course, implied that the three general experimental areas (section II, paragraph 1.a) could not be studied independently.

Without doubt, the development of an independent SiOH end group analysis was mandatory and absolutely essential to the success of this program. Consequently, all efforts were directed toward this end. An excellent end group analysis was in fact developed (section II, paragraph 1.d) and subsequently utilized to initiate studies of the three main process areas (sections II, paragraphs 1.e and 1.f).

c. Monomer Synthesis

There is a prevalent notion that high polymers can be prepared using conventional organic synthesis procedures. This is far from the truth; and, in fact, the monomers used in most large-scale polymerizations are among the purest known organic substances. Consequently, monomer synthesis and purification constitutes the major portion of any exploratory polymer program (up to 80 to 90 percent of the experimental work by many estimates). Fortunately, satisfactory procedures for the bisureidosilanes and $\underline{m}$-$C_2B_{10}H_{10}(SiMe_2OH)_2$ required for the present work have been previously developed at UCC. Nonetheless, we point out and emphasize that a large amount of our laboratory time must be spent in monomer preparation and purification (30 to 50 percent). Clearly, the availability of funds for technical assistance in monomer preparation would significantly impact the polymerization effort and hasten the availability of the high temperature adhesive.

At UCC the major task was to develop a satisfactory large scale industrial process for the preparation of carborane-siloxane polymers. Consequently, only those manipulations and purification techniques suitable for plant production were acceptable. On the other hand, the present program does not require large quantities of adhesive, and, therefore, the scope of the process options is significantly broadened and improvements in monomer purity can be envisioned. In the following sections, the UCC monomer synthesis processes used in this work,[3] as well as a few modifications implemented at Hughes, are described.

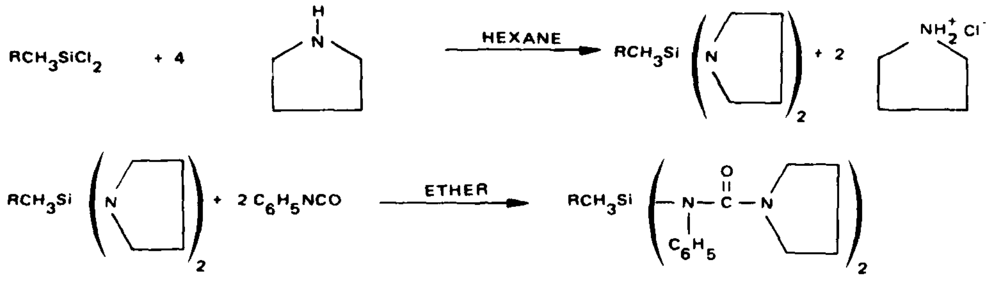
(1) Bisureidosilanes

In 1961, Pike[4] reported that diaminosilanes condense with disilanols to form polysiloxanes under extremely mild conditions where no self-condensation of silanols was observed. Incorporation of vinyl, phenyl, trifluoropropyl and other groups for crosslinking and specific property optimization was convenient. Subsequently, the aminosilane method became an important tool for polymer synthesis and was successfully utilized by several research groups for the preparation of block copolymers, arylene-siloxane polymers, ferrocene-containing siloxane polymers, and many others.[5]

Therefore, diaminosilanes were the initial comonomer choice for the preparation of linear carborane-siloxane polymers at Union Carbide. Linear polymer was indeed produced, but the molecular weight was limited ($\overline{M}_w$ ~18,000) by a demonstrated cleavage of the C-Si bond by the basic amine by-product of the polymerization reaction.[6] Subsequently, a variety of monomers were evaluated in which the by-product HX would be neutral. Ultimately, bisureidosilanes which generated an unreactive urea by-product during the condensation polymerization were prepared and found to be excellent reagents for the synthesis of high and ultrahigh molecular weight polymers. In particular, the N-phenyl-N'-pyrrolidinylurea unit consistently produced crystalline bisureidosilanes, whereas, oils were often obtained when other groups were employed.

Thus, bisureidosilanes emerged as the preferred comonomer because of their unique properties, which included the generation of a neutral by-product, enhanced reactivity compared to existing alternatives, and high purity capability because of their crystalline structure.

A variety of bisureidosilanes were prepared at UCC by the reaction of a diaminosilane with two equivalents of phenyl isocyanate in diethyl ether as shown below. Under carefully controlled conditions, the bisureidosilane crystallized (precipitated) directly from the reaction mixture and was isolated in good purity (>98 percent) simply by filtration and evaporation of solvent.



where:

$R = CH_3, C_6H_5$

Bisureidosilanes are extremely sensitive to moisture and a strictly inert atmosphere must be maintained at all times. Thus, it is essential that all reactants and solvents be rigorously purified and that all manipulations be carried out using Schlenk techniques and/or in an inert atmosphere Dry Box. A complete description of the inert atmosphere equipment and experimental techniques used throughout this program is included in the Appendix.

Even though the bisureidosilanes are in fact quite air sensitive, if they are handled correctly as discussed in the Appendix, they become routine monomers and present no more than the usual problems encountered with air sensitive intermediates in silicone polymer chemistry. However, a considerable amount of confusion has arisen concerning the stability and reactivity of bisureidosilanes. This can be attributed almost entirely to erroneous conclusions drawn from the estimation of purity by NMR using $CDCl_3$ as solvent. For example, Lenz and Dvornic[7] have reported that bisureidosilanes are "best" prepared at low temperatures (-20°C) and are not suitable for long term storage. This can be attributed to the fact that bisureidosilanes react with $CDCl_3$ producing what apparently is the urea by-product in solution (ca. 5 to 15 percent of the total mixture). This fact was demonstrated previously at UCC and confirmed in the present work. Thus, CD_2Cl_2 in a sealed tube is the solvent of choice for estimation of bisureidosilane purity by NMR. Furthermore, these compounds can be stored indefinitely if anhydrous conditions are maintained.

Synthesis of Bis(pyrrolidinyl)dimethylsilane. A 1000 ml three-necked flask was equipped with mechanical stirring, a thermometer, an addition funnel with the side arm closed, and two argon inlets. A solution of dichlorodimethylsilane (51.6 g, 0.4 mole) in n-hexane (450 ml) was transferred by double tipped syringe needle into the reaction vessel. Pyrrolidine (127 g, 1.79 mole) was placed in the addition funnel and added dropwise with stirring and cooling in an ice bath maintaining the addition rate so that the internal temperature did not exceed 10°C. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for 15 hours.

The reaction mixture was filtered through a coarse fritted-glass funnel into a Claisen flask set up for solvent removal and distillation. Most of the volatiles were removed by distillation at atmospheric pressure (bath temperature 100°C). After cooling to room temperature, the last traces of volatile material were removed in vacuo to a Dry Ice-acetone cooled receiver. The receiver was changed and the residual oil was distilled and gave 44.6 g (56 percent) of the product, bp 48-50°C (0.08 mm) [lit.[3] bp 59-60° (0.25 mm)].

Bis(pyrrolidinyl)dimethylsilane is a very strong base which reacts readily with most halogenated solvents and with tetramethylsilane, the usual NMR internal standard. Therefore, NMR spectra are best determined neat or in benzene-d_6 (rigorously dried). The NMR spectrum (neat) was consistent with the structure and no impurities were observed. Distillation immediately prior to the reaction with phenyl isocyanate is recommended.

Bis(pyrrolidinyl)methylphenylsilane was prepared in a similar manner in 55 percent yield, bp 100-102°C (0.06 mm) [lit.[3] bp 114-8°C (0.05 mm)].

Synthesis of Bis(N-Phenyl-N'-pyrrolidinylureido)dimethylsilane. A 1000 ml three-necked flask was equipped with mechanical stirring, thermometer, an addition funnel, and two argon inlets. The glassware was oven-dried (150°C) for 12 hours and allowed to cool in an inert atmosphere. Anhydrous diethyl ether (480 ml) and freshly distilled bis(pyrrolidinyl)-dimethylsilane (43.5 g, 0.21926 mole) was placed in the reaction flask. With stirring and cooling in an ice bath, phenyl isocyanate (52.2 g, 0.438 mole) was added dropwise over a two hour period while maintaining the internal temperature in the 0-5°C range. The reaction was moderately exothermic. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for four hours. Stirring was discontinued and the bisureidosilane was allowed to slowly crystallize overnight.

The ethereal slurry of the product was filtered through a coarse fritted-glass filter (equipped with vacuum stopcocks) into another 1000 ml, three-necked flask. Conventional Schlenk techniques were used throughout in order to insure an inert atmosphere. The solid product was dried in vacuo (bath temperature 50°C, 0.05 mm), taken into the Dry Box, ground to a fine powder, and stored in Schlenk tubes for use as required. The yield was 59.9 g (62 percent), mp 104-107.5°C [lit[3] mp 123-125°C]. Two crystalline forms of this compound which are thermally interconvertible are often obtained. The lower melting form (mp 104-107.5°C) is frequently obtained from diethyl ether while the higher melting form (mp 123-125°C) can be anticipated from hydrocarbon solvents. Their properties are identical in solution and in the polymerization reaction.

Bis(N-phenyl-N'-pyrrolidinylureido)methylphenylsilane was prepared in a similar manner in 71 percent yield, mp 97.5-100°C [lit[3] mp 98-101°C].

(2) *m*-Carborane Disilanol [*m*-$C_2B_{10}H_{10}(SiMe_2OH)_2$]

The synthesis of *m*-$C_2B_{10}H_{10}(SiMe_2OH)_2$ (Figure 2) has been extensively investigated at Olin [8] and at Union Carbide[3], and several alternative synthetic pathways have been developed. The UCC procedure shown below is, however, the preferred method for producing high purity, monomer grade disilanol since many of the disadvantages of the two alternative procedures developed by Olin, which involved vapor phase isomerization of *o*-carborane and recrystallization of the air sensitive *o*-$C_2B_{10}H_{10}(SiMe_2Cl)_2$, respectively, can be avoided.

m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ is a colorless, air stable, crystalline compound (mp 98-99°C) and was routinely purified at UCC by recrystallization from heptane and filtration in air. This procedure was deemed satisfactory and in fact led to high and ultrahigh molecular weight polymer. Subsequently, the possibility of silanol condensation at heptane reflux (98°C) and/or moisture pick-up in air were suggested as possibilities. Therefore, processing of this monomer was modified to include additional recrystallizations from *n*-hexane-benzene(3:1 v/v) (bp 61°C) and manipulation in an inert atmosphere. No changes were observed in the NMR spectrum and the melting temperature range (98-99°C). Moreover, the molecular weight obtained at the prepolymer stage was unchanged. Thus, existing methods appear to yield excellent monomer grade disilanol and further purification is not recommended.

Synthesis of m-$C_2B_{10}H_{10}(SiMeOH)_2$. A 5000 ml, three-necked flask was equipped with mechanical stirring, thermometer, a nitrogen inlet, and a 1500 ml pressure equalized addition funnel (with side arm closed). Water (2000 ml) and acetone (2000 ml of Fisher 99 mole percent) were charged to the reaction flask. Bis(chlorodimethylsilyl)-*m*-carborane (389 g, 1.18 mole) was placed in the addition funnel by syringe and added dropwise over a four hour period with stirring and cooling in an ice bath (0-10°C). Strictly anhydrous conditions are recommended until the silyl chloride is added to an *excess* of water. After completion of the addition, stirring was continued for 30 minutes and then the reaction mixture was transferred to a separatory funnel. The aqueous layer was extracted with four 250-ml portions of methylene chloride. The organic layer was then washed with water until the washings were neutral and dried over magnesium sulfate. After filtration, the solvent was evaporated giving the crude product (oil) which was further dried *in vacuo* (0.05 mm) to remove all volatile material.

The crude disilanol was recrystallized twice, first from 2000 ml of heptane and then from 1500 ml of fresh heptane giving 169 g (49 percent) of *m*-$C_2B_{10}H_{10}(SiMe_2OH)_2$, mp 99-98°C [lit[9] mp 98-99.5°C]; nmr ($CDCl_3$) 2.30 (S, 2H), and 0.025 ppm (S, 18H).

The substance was further purified by recrystallization three times from *n*-hexane-benzene (3:1 v/v). In each case a small quantity of solvent was removed by distillation in order to remove any residual moisture by

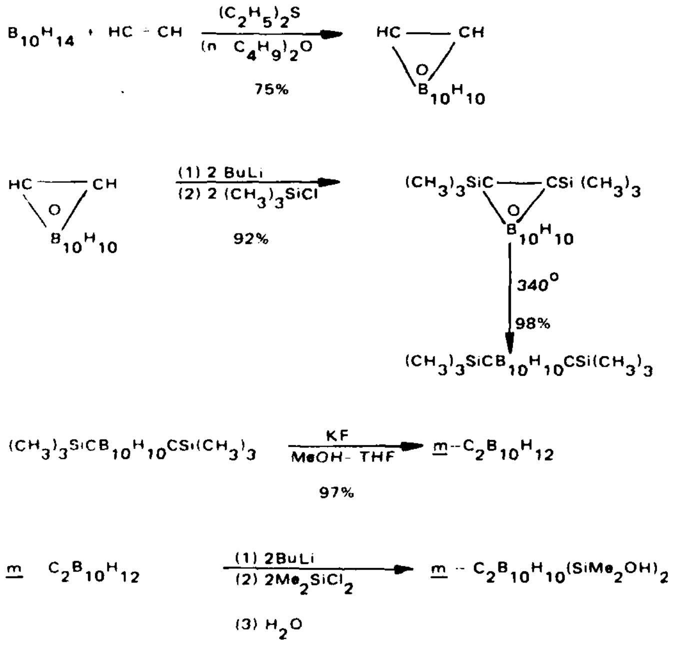

B10H14 + HC ≡ CH
(C2H5)2S
(n C4H9)2O
75%
HC — CH
O
B10H10
(1) 2 BuLi
(2) 2 (CH3)3SiCl
92%
(CH3)3SiC — CSi (CH3)3
340°
98%
(CH3)3SiCB10H10CSi(CH3)3
KF
MeOH- THF
97%
m-C2B10H12
(1) 2BuLi
(2) 2Me2SiCl2
(3) H2O
m - C2B10H10(SiMe2OH)2

FIGURE 2. UCC PROCEDURE FOR m-CARBORANE DISILANOL

azeotropic distillation. Anhydrous conditions were strictly maintained throughout. The hot solution was filtered and the product was allowed to slowly crystallize at ambient temperature. The final compound was filtered and dried in vacuo (50°C bath temperature, 0.05 mm) for 24 hours and stored in the Dry Box and used as required. The final melting temperature was 98-99°C.

d. Prepolymer End Group Analysis

In the UCC technology, the presence of active SiOH sites in the prepolymer was qualitatively judged by the ability to accomplish the molecular weight advancement as discussed in section II, paragraph 1.f. Quantitative corroboration was obtained by active hydrogen analysis. The analytical method consisted of reacting the sample with CH_3MgBr or CH_3Li and measuring the amount of methane evolved by gas chromatography as shown. However,

$$\textcircled{P} - SiMe_2OH + CH_3MgBr \longrightarrow \textcircled{P} - SiMe_2OMgBr + CH_4\uparrow$$

the active hydrogen technique is probably not valid in the present system for a number of reasons. First, as Sorenson and Campbell[10] have pointed out, most conventional end group analyses are unreliable when the molecular weight is greater than 25,000. Second, nucleophilic attack at the carboranyl C-Si bond, without the evolution of methane may compete with the normal reaction; and finally, most of the prepolymer samples contain a small quantity of the urea by-product which is very difficult to remove by fractional precipitation and reacts with the Grignard reagent to produce methane.

Therefore, the development of a new end group analysis sufficiently sensitive for our needs presented a truly formidable challenge. A literature review suggested that theoretically there were numerous possibilities, many of which had been applied to low molecular weight polydimethylsiloxanes. In particular, the use of NMR to determine sequence lengths of polymers is well established.[11] Natural abundance ^{1}H, ^{13}C, and ^{29}Si Fourier Transform NMR have been successfully employed for relatively low molecular weight polydimethyldisiloxanols.[12] However, NMR was not promising for the present work because of the low concentration of end groups and the high viscosity of the polymer solutions. Similarly, all methods based on conventional OH chemistry such as the Grignard method and tritium exchange were not suitable because of the necessary rigorous purification of the prepolymer prior to analysis. By the process of elimination, UV and Fourier transform IR (FT-IR) spectral analysis emerged as the only feasible analytical procedures, taking into account the limited scope of this program. No significant spectral differences between end groups and the remainder of the polymer chain were observed, however. Therefore, derivatization and subsequent analysis was much more promising. A list of essential and some desirable characteristics of an ideal derivatization end group analysis is compiled in Table 1.

TABLE 1

CRITERIA FOR A SUCCESSFUL DERIVATIZATION END GROUP ANALYSIS

Essential Criteria

- Quantitative derivatization reaction
- No significant interferences
- Efficient removal of excess end capping reagent
- Availability of a quantitative trace analysis method for end capped prepolymer (10^{-5} - 10^{-6} M in end groups)

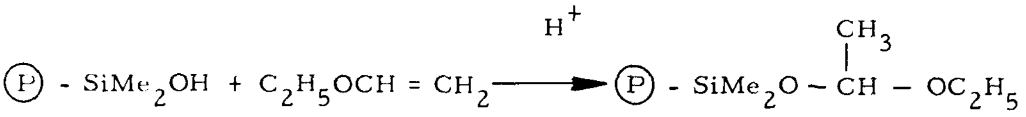
Desirable criteria

- Reasonable synthetic accessibility of derivatization reagent
- Formation of a hydrolytically stable linkage for quantitative analysis
- No elaborate experimental manipulations for end group analysis; must be routinely performed

(1) Ethyl Vinyl Ether End Capping

Examination of the literature suggested that ethyl vinyl ether was a promising candidate reagent. For example, Me_3SiOH and $C_2H_5OCH = CH_2$ reacted readily in the presence of an acid catalyst to give the unsymmetrical acetal in 40 percent yield, however, $C_6H_5SiMe_2OH$ reacted analogously in 93 percent yield.[13] This is in general accord with the concept that aliphatic silanols are sensitive to acid catalyzed condensation, whereas, aromatic (and carborane) silanols are not. The analysis for carboranyl SiOH was envisioned and tested experimentally as follows.

Step 1. SiOH Reaction With Ethyl Vinyl Ether



$$\textcircled{P} - SiMe_2OH + C_2H_5OCH = CH_2 \xrightarrow{H^+} \textcircled{P} - SiMe_2O - \overset{\overset{CH_3}{|}}{CH} - OC_2H_5$$

Exploratory NMR studies in which m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ was treated with an excess of ethyl vinyl ether in benzene-d_6 in the presence of a catalytic amount of p-toluenesulfonic acid confirmed that the reaction proceeded in quantitative yield at room temperature. The reaction was subsequently carried out on a larger scale to permit isolation and characterization of the product as follows:

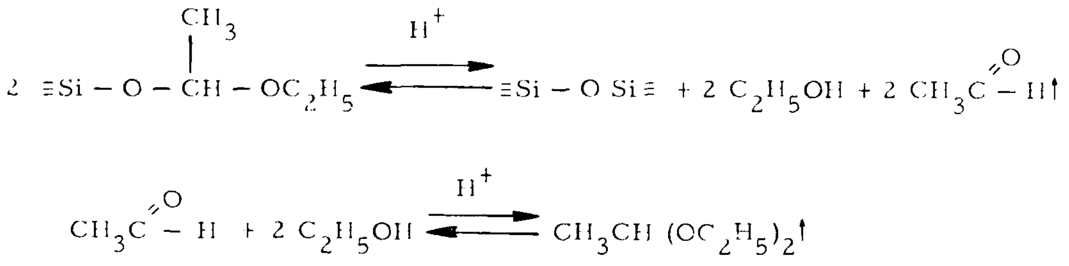
$$\underline{m}\text{-}C_2B_{10}H_{10}(SiMe_2OH)_2 + \underset{\text{(excess)}}{C_2H_5OCH{=}CH_2} \xrightarrow[C_6H_6]{H^+}$$

$$\underline{m}\text{-}C_2B_{10}H_{10}\left(SiMe_2OCH(CH_3)OC_2H_5\right)_2$$

Synthesis of *m*-$C_2B_{10}H_{10}(SiMe_2OCH(CH_3)OC_2H_5)_2$. A 100 ml three-necked flask was equipped with magnetic stirring, an addition funnel and an argon inlet. A solution of *m*-$C_2B_{10}H_{10}(SiMe_2OH)_2$ (5.0 g, 0.017 mole) and ethyl vinyl ether (3.08 g, 0.0428 mole) in dry benzene (75 ml) was placed in the addition funnel and added dropwise over a period of 30 minutes to a solution of *p*-toluenesulfonic acid (1 mg) in benzene (5 ml) with stirring and cooling in an ice bath After completion of the addition, the homogeneous reaction mixture was stirred for 18 hr at ambient temperature under argon and then filtered through a small amount of silica gel to remove the acid catalyst. The solvent was evaporated and the pale yellow residual oil was distilled giving 5.15 g (69 percent) of the colorless product [bp 140-142°C (0.09 mm)]. The NMR and IR spectra was consistent with the structure and no impurities were observed.

Step 2. Removal of Excess Ethyl Vinyl Ether and the Acid Catalyst

Complete removal of the acid catalyst was necessary in order to suppress the formation of volatile products catalyzed by acid during vacuum treatment. Several methods for removal of the acid catalyst were investigated as follows:



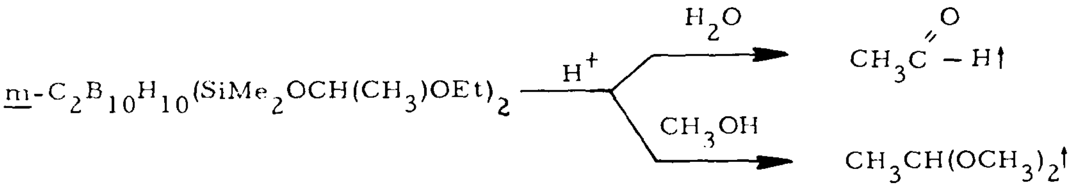
$$2\ \equiv Si-O-\overset{CH_3}{\overset{|}{CH}}-OC_2H_5 \overset{H^+}{\rightleftharpoons} \equiv Si-O\ Si\equiv\ +\ 2\ C_2H_5OH + 2\ CH_3\overset{O}{\overset{\|}{C}}-H\uparrow$$

$$CH_3\overset{O}{\overset{\|}{C}}-H\ +\ 2\ C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3CH\ (OC_2H_5)_2\uparrow$$

- Chromatography (filtration) on silica gel and neutral alumina was effective but tedious. Material losses were significant and an inert atmosphere was essential.
- Rapid wash with cold water failed because of the hydrolytic sensitivity of the product.
- Use of a macroreticular ion exchange resin[14] containing strongly acidic SO_3H groups as catalyst which could be removed by simple filtration. This catalyst gave none of the expected product.

Thus, the only approach developed was filtration through silica gel. Removal of the excess ethyl vinyl ether *in vacuo* was then satisfactory.

Step 3. Acid Catalyzed Removal of End Capping Group and Quantitative Determination of Aldehyde or Acetal Liberated



$$m\text{-}C_2B_{10}H_{10}(SiMe_2OCH(CH_3)OEt)_2 \xrightarrow{H^+} \begin{cases} \xrightarrow{H_2O} CH_3C(=O)-H\uparrow \\ \xrightarrow{CH_3OH} CH_3CH(OCH_3)_2\uparrow \end{cases}$$

Excellent trace colorimetric methods for the determination of acetaldehyde[15] and its acetals[16] have been developed. Thus, in the present analysis, acid catalyzed treatment of the end capped polymer and vacuum collection of either acetaldehyde or $CH_3CH(OMe)_2$ depending on the analytical method chosen was envisioned.

Somewhat reluctantly at this point, the vinyl ether end capping technique was abandoned, because solving the following technical problems within the scope of the program was doubtful:

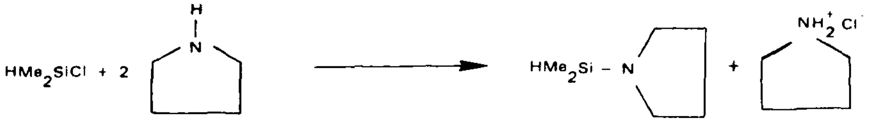
- The end capped adduct linkage ($SiOCH(CH_3)OEt$) was hydrolytically sensitive and small amounts of the capped prepolymer were difficult to handle.
- A satisfactory method for removing the acid catalyst from small amounts of prepolymer was not developed. (Step 1.)
- Interference by residual urea by-product in the prepolymer was confirmed. Removal of this contaminant would be tedious.

(2) Dimethylsilylureidosilane End Capping

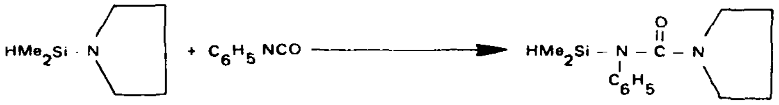
Attention was directed toward a derivatization reaction utilizing the same chemistry developed for both the prepolymer preparation and the advancement reaction as shown in section II, paragraph 1.d(2)(d). Thus, a stable Si-O-Si linkage is produced, the urea by-product and traces of water and methanol do not interfere, and quantitative derivatization is anticipated in view of the demonstrated efficiency of the bisureidosilane polymerization. The selection of group R, however, was not straightforward. Synthetic accessibility, excess reagent removal and the method of analysis were given careful consideration. Ultimately, $HMe_2SiN(C_6H_5)CON(CH_2)_4$ was selected as the best candidate reagent meeting all of the criteria in Table 1. These postulates were tested and confirmed experimentally as follows.

(a) Derivatization Reagent Synthesis

$HMeSi[N(C_6H_5)CON(CH_2)_4]_2$ was prepared at UCC[3] and used to provide crosslinking sites in the polymer chain, therefore synthetic problems involving the SiH bond were not expected. The conventional bisureidosilane synthesis was utilized with only a few modifications.



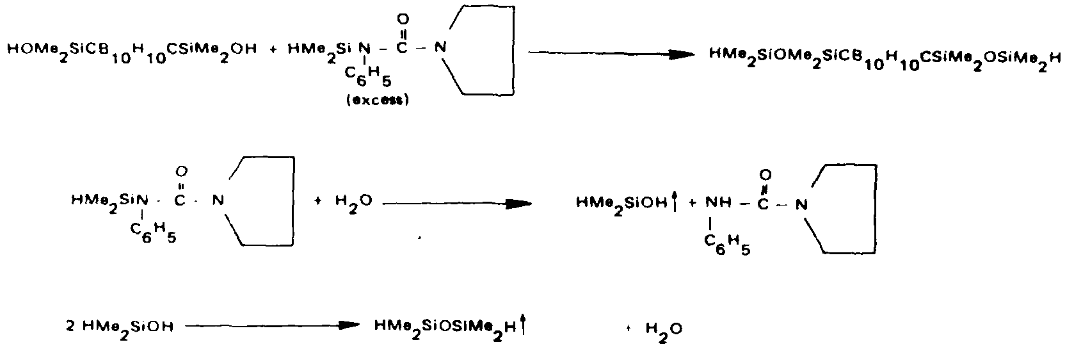
Synthesis of Dimethylsilylpyrrolidine. The experimental procedure outlined in section II.1.3.1 was employed. Thus, dimethylchlorosilane (82.4 g, 0.87 mole) was treated with pyrrolidine (124 g, 1.74 mode) in pentane (450 ml) at 0-10°C. After filtration and distillation, dimethylsilylpyrrolidine [66.5 g (59 percent); bp 123-125°C (760 mm)] was obtained as a colorless liquid.



Synthesis of (N-Phenyl-N'-pyrrolidinylureido)dimethylsilane. The procedure outlined in section II, paragraph 1.c(1) was employed. A 250 ml three-necked flask was equipped with a septum, a thermometer, a magnetic stirring bar, an addition funnel with the side arm closed, and two argon inlets. A solution of dimethylsilylpyrrolidine (25.7 g, 0.199 mole) in diethyl ether (75 ml) was transferred into the reaction vessel by syringe. Phenyl isocyanate (25.3 g, 0.214 mole, ~7 percent excess) was placed in the addition funnel and added dropwise over one hour while maintaining the internal temperature in the 0-10°C range by external cooling (ice bath). After completion of the addition the cooling bath was removed and the reaction mixture was stirred at room temperature for 14 hours. The crystalline product was filtered under an inert atmosphere, dried in vacuo, transferred to a large sublimation apparatus, and vacuum sublimed (bath temperature 85°C, 0.09 mm). The crystalline product (mp 78-80°C) was ground to a fine power and stored in the Dry Box for use as required. The compound could be distilled [bp 105-7°C (0.07 mm)], but easily clogged the distillation flask.

(b) Model Compound Preparation

A model compound was prepared from m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ and dimethylsilylureidosilane in order to test the criteria set forth in Table 1 before proceeding to the prepolymer samples. Exploratory NMR studies indicated that the reaction proceeded in quantitative yield at ambient temperature as shown and also that the excess reagent was effectively removed by hydrolysis and vacuum pumping. Dimethylsilylureidosilane reacted rapidly with water giving dimethylsilanol which disproportionated rapidly to dimethylsilyl ether. Both compounds are quite volatile and readily removed by vacuum treatment.


HOMe$_2$SiCB$_{10}$H$_{10}$CSiMe$_2$OH + HMe$_2$Si N – C – N
O
C$_6$H$_5$
(excess)
HMe$_2$SiOMe$_2$SiCB$_{10}$H$_{10}$CSiMe$_2$OSiMe$_2$H
HMe$_2$SiN · C · N
C$_6$H$_5$
+ H$_2$O
HMe$_2$SiOH↑ + NH – C – N
2 HMe$_2$SiOH
HMe$_2$SiOSiMe$_2$H↑
+ H$_2$O

Synthesis of m-$C_2B_{10}H_{10}(SiMe_2OSiMe_2H)_2$. A 100 ml three-necked flask was equipped with an addition funnel, a magnetic stirring bar, and an argon inlet. A solution of m-$C_2B_{10}H_{10}(SiMe_2OH)_2$ (2 g, 0.00685 mole) in diethyl ether (25 ml) was added dropwise over one hour to a solution of dimethylsilylureidosilane (6.8 g, 0.0274 mole) in diethyl ether (25 ml) at 25°C with stirring. After completion of the addition, the reaction mixture was stirred for 15 hours, treated with water (10 ml) and stirred for an additional 45 minutes. After filtration and separation of layers, the ether layer was washed with water (25 ml) and dried over $MgSO_4$. After filtration and evaporation of solvent, distillation of the residual oil gave 2.18 g (78 percent) of the product [bp 123-125°C (0.05 mm)]. The NMR and IR spectra were consistent with the structure and did not reveal the presence of impurities. The compound has been prepared previously from m-$C_2B_{10}(SiMe_2CH)_2$ and HMe_2SiCl.[17] In summary, the model compound studies confirmed all of the criteria for an end group analysis with the exception of quantitative analysis by FT-IR.

(c) Quantitative Trace Analysis by FT-IR

At this point it was necessary to demonstrate that the silane end caps (SiH) could be detected quantitatively and in trace concentrations. Anticipation of the required detection sensitivity in prepared prepolymers can be arrived at as follows:

Let:

m prepolymer specimen weight available = 10. g/ℓ

Sensitivity min. detectable fraction of prepoly. silanol terminated ≈ 0.01

Threshold conc. of silanol terminated prepolymer: 0.01 x 10 = 0.1 g/ℓ

$\overline{M}_N$ = number average molecular weight of prepolymer ≈ 5 x 10^4

∴ Estimated sensitivity threshold:

$$\frac{0.1}{5 \times 10^4} \approx 2 \times 10^{-6} \text{ moles prepoly.}/\ell$$

In the case of the model compound it is assured that each molecule will have a SiH end cap at each end. Thus the expected minimum concentration, in terms of SiH equivalents, is equal to twice the molarity, i.e., 4×10^{-6} SiH equiv./ℓ.

The original basis for selecting an SiH end cap was the observation that in the IR spectrum of the prepolymer the SiH band (located at 2130 cm^{-1}) was very strong and clear of interferences from other bands. Using a Nicolet MX-1 Fourier transform infrared spectrometer (FT-IR), it was soon observed, however, that even with the end capped model compound, in solution in CCl_4 (with the solvent spectrum "subtracted" out), the SiH absorption band was almost completely masked by an Si-O overtone at 2048 cm^{-1}. This problem was remedied by first generating a spectrum of the parent silanol compound and then "subtracting" this spectrum from the subsequent spectrum of the silane-terminated compound. The result was a clear display of the absorbance (A) of the SiH band at the measured concentration (c, in moles compound/ℓ) and liquid cell path length (b, in cm).

Two solutions of the SiH end capped model compound in CCl_4 were prepared, the concentrations differing by a factor of ten and in the regime of interest. Each solution specimen was transferred separately into a 3 mm sodium chloride liquid cell (variable path length, RIIC, England). The 3 mm path was necessary for adequate sensitivity because of the very low SiH concentration. Each solution specimen was run in conjunction with a control (a CCl_4 solution of the parent silanol at a concentration similar to that of the model compound). Individual spectra for each specimen and its control were obtained after 128 scans in the absorbance mode. After "subtraction" of the control spectrum, absorbance (A) values were measured as follows:

(SiH Concentration), equiv./ℓ	A (Absorbance)
2.91×10^{-5}	1.7×10^{-3}
2.91×10^{-4}	1.67×10^{-2}

Based on the previous complete characterization (section II, 1.d(2)(b); by boiling point, NMR, IR, and elemental analysis) of the model compound as indeed the dual SiH end capped derivative of the parent $\underline{m}$-carborane disilanol, the measured scaling of A with c (above) represents verification of the quantitative end group analysis at trace concentration levels of interest. Corresponding values of A and c can be used to evaluate the molar absorptivity ε (also termed molar absorption coefficient) as follows:

$$A = \epsilon b c$$

Rearranging: $$\epsilon = \frac{A}{bc} = \frac{1.7 \times 10^{-3}}{(0.3)(2.91 \times 10^{-5}/2)} = 390 \ \ell/\text{mole-cm}$$

where:

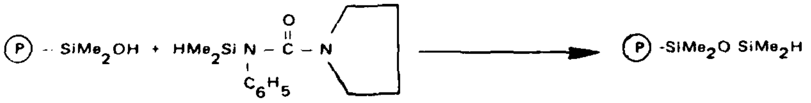
b = 0.30 cm (from interference measurement)

c = concentration, in moles compound/ℓ

$= \frac{\text{equivalents of SiH}/\ell}{2}$

By means of this value of ϵ, the value of b, and the measured value of A, the concentration of OH groups (as indicated by the SiH derivative, i.e., 1 OH = 1 SiH) can be determined in the free silanol fraction of the prepolymer. This conclusion is based on the assumption that, since the linkage (carborane – Si-O-Si-H) in the model compound and in the prepolymer are similar, ϵ is the same in both. It is therefore further concluded that the criteria (Table 1) for a successful derivatization end group analysis have been satisfied.

(d) Prepolymer SiOH Analysis



Procedure. A 100 ml single-necked (24/40), round bottomed flask was equipped with a side arm and Teflon stopcock, a septum, and a magnetic stirring bar under an inert atmosphere. The prepolymer (1392-5, 0.140 g, RV 0.48) was weighed into the flask and toluene (2.5 mil) was added by syringe. In another similarly equipped flask were placed dimethylsilylureidosilane (0.140 g - 0.00056 mole; large excess) and toluene (2.5 ml). The resulting solution was transferred by syringe to the flask containing the prepolymer solution in a single portion. The reaction mixture was stirred for 14 hours at ambient temperature. Distilled water (2 ml) was added and the reaction mixture was stirred for 45 minutes, filtered to remove urea by-product, and placed in a separatory funnel. The aqueous layer was removed and discarded, and the toluene solution of the product was added to a 10 fold excess of methanol (50 ml) with stirring over 15 minutes. The methanol (cloudy) was decanted and discarded, and the gummy residue was dissolved in CH_2Cl_2 (2 ml) and transferred to a flask for drying. Most of the volatiles were removed rapidly in vacuo to a Dry-Ice-acetone cooled receiver. The end capped polymer was dried in vacuo for 15 hours (bath temperature 50°C, 0.05 mm) giving 0.1244 g of product (∼89 percent recovery).

Analysis by FT-IR was carried out as follows:

1) Accurately weigh 100-200 mg of end capped prepolymer into a 10 ml volumetric flask.

2) Add spectral grade CCl_4 to the flask in (1). Dissolve prepolymer. Make up volume to 10 ml mark.

3) Repeat (1) and (2) with parent prepolymer to provide a control.

4) Add sufficient solution (2) to fill a clean, 3 mm, liquid, NaCl cell. Obtain the IR spectrum in a FT-IR.

5) Re-clean cell and repeat step (4) with solution (3).

6) Program FT-IR to subtract spectrum in step (5) from that in step (4).

e. Prepolymer Synthesis

For most of this effort the UCC preparation procedure, involving a heterophase reaction between solid monomers was followed. In contrast, considerable effort was devoted toward study of the effect of work-up parameters on the advanceability of the resultant prepolymer. When it could be demonstrated that work-up and isolation procedures exert little or no effect on prepolymer advanceability (i.e., on silanol content), then attention was directed at the reaction process.

(1) UCC Heterophase Reaction

The heterophase reaction employed is outlined in Figure 1. The mixed bisureidosilane solids are added incrementally (over an extended period of 4 hours) to a slurry of carborane disilanol solid in a limited volume of chlorobenzene solvent, the slurry being stirred and held at a low temperature (-10 ±5°C in the case shown). In this procedure, it appears that the reaction rate is controlled by the limited solubility of both monomers in the restricted volume of solvent available. Typical process parameters used in the Hughes prepolymer preparation runs (1392-5 through 1392-25; using the UCC procedure) are given in Table 2.

(2) Effect of Workup Parameters

Referring to Figure 1, it is noted that the reaction mass consists of prepolymer in the liquid phase and the urea by-product dispersed as a solid phase. The reaction mass (at room temperature) is first diluted with chlorobenzene and filtered to remove urea solids. Crude prepolymer is recovered (precipitated from the chlorobenzene phase) by adding the filtered chlorobenzene to methanol in the ratio 1 vol. ϕCl: 10 vol. CH_3OH. Acetonitrile, CH_3CN, may be used instead of CH_3OH as a precipitating solvent.

TABLE 2

PREPOLYMER PREPARATION PARAMETERS

Parameter		Batch			
		1392-5	1392-11	1392-13	1392-17
Suspension Medium	Solvent	ϕCl	ϕCl	ϕCl	ϕCl
	ml solvent/g disilanol	6.2/6.0	6.2/6.0	6.2/6.0	8.0/6.2
External bath temperature, °C		-10	-23	-23	-23
Disilanol/bisureidosilane mole ratio		1.06/1.0	1.06/1.0	1.06/1.0	1.06/1.0

Decantation of the liquid phase yields the prepolymer gum. This gum is next dissolved in CH_2Cl_2, reprecipitated (from CH_3OH or CH_3CN), and recovered by decantation of the liquid phase. Re-solution in CH_2Cl_2 is repeated, followed by precipitation and recovery. Vacuum drying to remove residual solvents from the prepolymer (gum) is the final work-up step. Such drying may be performed at room temperature or above ($\leq$100°C).

Optional washes of the initial chlorobenzene filtrate were deemed appropriate to remove potential end capping and otherwise degrading impurities and residual reactants. Those washes investigated included water, glacial acetic acid, and buffer solutions. In regard to silanol content, comparison of UCC conditions, e.g. 1392-9 and -23A, with acidic washes, e.g., 1392-13 and -23B, in Table 3 reveals no consistent benefit. The higher silanol content observed in 1392-13 was apparently a random event since it could not be repeated. In addition to those combinations of work-up parameters shown in Table 3 a portion of K1392-19B was redissolved in toluene to which was added glacial acetic acid. After stirring (1 hr), this solution was next washed with water and then with buffered solution (pH = 7.0). The washed toluene solution was then dried over $MgSO_4$, after which it was filtered. Finally, it was vacuum dried (50°C/18 hrs) to remove solvent. The resultant specimen was designated 1392-19B-1 and represents the effect of acid wash on the post-work-up prepolymer. Unfortunately, the effect on silanol content was not impressive.

The effect of changing the precipitating nonsolvent from methanol to acetonitrile is also displayed in Table 3. For example, compare specimens -18A and -19A. Little change is noted.

It was believed that prepolymer silanol content (and hence advanceability) was sensitive to thermal exposure during drying. Comparison of specimens 1392-5 with -18A and 1392-19A with -19B reveals no such thermal dependence.

Conclusions drawn from this investigation of work-up parameters are as follows:

- Acid treatment of the prepolymer, either during initial work-up or after work-up, is not a factor in determining silanol content.

- The medium used to precipitate prepolymer from the reaction solvent does not appear to be a determining factor.

- Heating during work-up does not appear to be a major factor.

Thus, the experimental evidence clearly indicates that the non-reproducible (and typically low) silanol contents in the prepolymer are not related to work-up and isolation procedures.

In an attempt to further narrow the area of search, a batch of prepolymer reaction mixture (K-1392-25) was end-capped (with the ureidosilane analytical reagent) prior to workup. Subsequent end group analysis

TABLE 3

EFFECT OF PREPOLYMER WORKUP CONDITIONS ON SILANOL CONTENT

Workup Parameters	Prepolymer Batch										
	1392-5	-9	-11	-13	-23B	-23A	-18A*	-18B*	-19A*	-19B*	-19B-1
Water wash of filtrate	Yes	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	***
Acetic acid treatment of filtrate	No	No	No	Yes	Yes	No	No	No	No	No	Yes
Buffer solution (pH=7.0) wash of filtrate	No	No	Yes	Yes	Yes	No	No	No	No	No	***
Precipitating medium	MeOH	MeOH	MeOH**	MeOH	MeOH	MeOH	MeOH	MeOH	CH_3CN	CH_3CN	–
Heating during workup	Yes (dry at 100°C/ 24 hr)	Yes (dry at 50°C/ 48 hr)	No	No	Yes (dry at 50°C/ 24 hr)	Yes (dry at 50°C/ 24 hr)	No	Yes (80°C/ 6 hr; 60°C/ 12 hr)	No	Yes (90°C/ 6 hr; 60°C/ 12 hr)	Yes***
RV, dl/g (25°C)	0.48	0.37	0.76	0.75	0.42	0.42	0.35	0.35	0.35	0.35	0.35
Silanol content, % of theo.	10	4	7	25	7	9	14	–	16	13	16

*Workup of aliquot of prepolymer K1392-17.
**Purified.
***Postworkup. See text.

revealed a silanol content of ~7 percent, typical of most previous efforts. This result further confirms the fact that the prepolymer silanol content is determined during the preparation stage.

The procedure for estimating silanol content in the prepolymer after workup is best illustrated by an example. In the case of prepolymer specimen 1392-5, its number average molecular weight $\overline{M}_N$ was estimated as 4.5×10^4 based on a measured RV = 0.48 (see section II, paragraph 2.c. later). The silane end capped derivative was made and designated 1393-57-1. A quantity of 0.1244 g of this derivative dissolved in 10.0 ml of CCl_4 displayed an absorbance A = 0.0033 at 2130 cm^{-1}.

$$\text{Meas. Silanol Conc. (by FT-IR)} = \left(\frac{A}{\epsilon .\ b}\right)\ell = \frac{(0.0033)\ 2}{(390)\ 0.3}$$

$$= 5.65 \times 10^{-5}\ \frac{\text{Equiv. SiH}}{\ell}$$

$$\text{Theo. Available Silanol} = \left(\frac{0.1244\ \text{g}}{4.5 \times 10^{4}}\right) 2 \left(\frac{1000\ \text{m}\ell/\ell}{10\ \text{m}\ell}\right)$$

$$= 55.3 \times 10^{-5}\ \frac{\text{equiv. SiH}}{\ell}$$

$$\text{Silanol Content} = \frac{5.65 \times 10^{-5}}{55.3 \times 10^{-5}} \times 100 = 10\%\ \text{(of theo.)}$$

(3) Homogeneous Reaction

A major departure was made from the UCC heterophase reaction. A larger volume of toluene was substituted for chlorobenzene as the reaction solvent in order to permit better control of the bisureidosilane addition rate. The bisureidosilane (as a solution in toluene) was added dropwise with stirring to the mostly dissolved carborane disilanol in toluene at -78°C over a period of one hour, such that at the end of the addition, the solution was nearly homogeneous. Stirring was continued for one hour. Next the -78°C bath was replaced with an ice bath, and stirring was continued. After 2 hours at ~0°C, aliquot No. 1 (1392-27A) was taken from the reaction mixture. After 2 more hours of stirring at ~0°C, aliquot No. 2 (1393-58-6) was taken from the reaction mixture. Stirring was continued, and the reaction mixture was allowed to warm gradually, to ~20°C in 15 hours. After conventional workup, the reaction product was end-capped for IR analysis (-58-7).

The above preparation procedure was repeated to yield an end-capped product for analysis labeled 1393-58-8. The results of these prepolymer preparation experiments are given in Table 4 along with data for advanceable UCC prepolymers. Review of these data yield the following tentative conclusions:

- Revised preparation procedures can yield high silanol contents (similar to that for known advanceable species) in a reproducible manner. (Compare -58-7 with -58-8)
- In an area of polymer chemistry plagued by random results, this first clue to reproducibility is an important advance.
- Lower RV values resulting from the above changes in preparation conditions do not preclude advancement to desired ultimate RV values of the order of 3. to 4.

TABLE 4

COMPARISON OF SILANOL CONTENT OF PREPOLYMERS PREPARED BY HOMOGENEOUS REACTION WITH KNOWN ADVANCEABLE UCC PREPOLYMERS

Parameter	Prepolymer						
	UCC 11233 71	UCC 11592 1	UCC 10615-67	1392 27A No. 1 Aliq.	1393-58 6 No. 2 Aliq.	1393 58-7 Product	1393 58 8 Product
Description	Advanceable prepolymer	Advanceable prepolymer	Advanceable prepolymer	See text	See text	See text	Repeat of 58 7
RV	0.97	0.98	0.52	0.01	0.08	0.11	0.08
Silanol content, % of theo	50	35.	35.	—	48.	46.	50

f. Molecular Weight Advancement

An important program goal at UCC was the preparation of block copolymers consisting of a polysulfone hard block (high Tg) and a carborane-siloxane soft block (low Tg), since considerable success had been achieved at UCC (Bound Brook) in the area of polysulfone-polydimethylsiloxane block copolymers, carborane-siloxanes were expected to provide an ideal soft block because of their thermoxidative resistance and low Tg values. Silanol terminated polydimethylsiloxanes were prepared in the molecular weight range 15,000 by using a stoichiometric excess of one of the comonomers.

Thus, an exploratory experiment was carried out using a 6 percent, excess of disilanol exactly as outlined in Figure 1. A silanol terminated prepolymer, $\overline{M}_w$ 20,000 was theoretically predicted, however, a much higher molecular weight compound ($\overline{M}_w$ 140,000) was in fact obtained after hydrolysis and work-up. This was attributed to the heterophase reaction conditions and to the poor solubility of disilanol in chlorobenzene. To determine if the prepolymer still contained silanol groups, a chlorobenzene solution was slowly titrated with additional bisureidosilane (Figure 1). A large increase in viscosity and precipitation of the sparingly soluble ultrahigh molecular weight polymer was observed. Repetition of the experiment using a 12 percent excess of disilanol gave an analogous result.

Subsequent attempts a year later to reproduce the ultrahigh molecular weight polymer preparations were not particularly successful. Advancement could be accomplished on approximately 20 percent of the available prepolymer samples. Since we had no previous experience at Hughes with the advancement reaction, a top priority experiment was to advance a UCC prepolymer sample (UCC 11233-71) which had previously been advanced at UCC from an RV 1.04 to 3.2. This sample was stored for about two years prior to this experiment. A chlorobenzene solution of the prepolymer was slowly titrated with methylphenyl bisureidosilane. After workup and precipitation from methanol the RV was unchanged. This could be attributed either to decomposition of silanol groups during storage or more likely to a nonreproducible advancement procedure. Thus, doubt about the reliability of the advancement clearly demanded an intensive effort to develop a silanol end group analysis (section II, paragraph 1.d).

Subsequently, end group analysis (Table 4) indicated that the UCC sample (UCC 11233-71) did indeed have high silanol content. Similarly, analysis of the recovered material (1393-57-7) from this unsuccessful attempt confirmed that high silanol content had been retained. A second advancement attempt therefore was carried out on the recovered sample, and in contrast to the first attempt, a slower titration of the prepolymer with bisureidosilanes and a higher reaction temperature (65°C) was employed. The sample advanced from RV = 0.91 to RV = 1.43, which was admittedly less than hoped for, but was nonetheless encouraging.

An attempt to advance one of the low RV, high silanol content prepolymer specimens (1392-27C) extended the RV from 0.11 to 0.88. Again this was encouraging. Unlike the case above (UCC 11233-71), the silanol content in this case unfortunately dropped from 48 to 13 percent after advancement, with no ready explanation apparent.

In summary, the scope of our work in the area of molecular weight advancement has not been extensive thus far, however, some comments and preliminary conclusions upon which future research can be based are as follows:

- The advancement step is not generally reliable as suggested by UCC studies.
- A meaningful investigation of the advancement reaction must await the definition of a reproducible process for the preparation of prepolymers containing high silanol content.
- It has been demonstrated (section II, paragraph 1.e) that prepolymer workup conditions do not determine silanol content: however, control of these variables may be crucial to a successful advancement (e.g., incomplete drying, introduction of trace impurities during precipitation, etc.).
- Rapid addition of bisureidosilanes may result in "overtitration" and quenching of the advancement reaction. The adjustment of stoichiometry is difficult and at least some general information concerning the rate of polymerization must be obtained.

2. POLYMER CHARACTERIZATION

Two techniques have been used to follow the molecular weight of synthesized materials, namely gel permeation chromatography (GPC) and dilute solution viscometry. The procedure has been to simultaneously employ GPC and solution viscosity methods in order to establish a correlation between the two. If this could be accomplished, then the simpler solution viscosity technique could be used for screening purposes (i.e., to support the synthesis effort). For this purpose, measurements were made on materials prepared during the current program as well as on UCC research materials produced during the period 1976-1978. Reduced viscosity (RV) measurements were made at Hughes and UCC. GPC measurements were made at Hughes Aircraft (Malibu Research Laboratory; courtesy Dr. Leroy Miller), University of Massachusetts (courtesy Dr. R. W. Lenz), and Union Carbide Corporation (Chemicals and Plastics Laboratory; Dr. F. H. Covitz). Comparative data covering a broad range of prepolymer and polymer molecular weights are presented in Table 5. These data are arranged in order of increasing RV values.

a. Gel Permeation Chromatography

Weight average molecular weight, $\overline{M}_W$, number average molecular weight $\overline{M}_N$, and polydispersity, $\overline{M}_W/\overline{M}_N$, were determined in a gel permeation chromatograph. The apparatus consisted of several columns in series, each packed with crosslinked polystyrene of different, selected pore sizes. In these investigations, tetrahydrofuran was the common solvent used, i.e., for swelling (equilibrating) the packing, for making the polymer solutions to be analyzed, and for the elution solvent (elutant). Prior to analyzing the unknown solutions, a calibration curve was generated. It was obtained (point by point) by injecting a series of different monodisperse polystyrene solutions (i.e. polystyrene of a single known molecular weight) into the column, the solvent being the same as the elution solvent. Any given molecular weight fraction (polystyrene) was removed from the column by a narrow fraction of elutant. Each such fraction provided a single point on the calibration curve. Thus a sufficient number of polystyrene fractions were used to establish a calibration curve covering the molecular weight range of interest. Following calibration, the unknown material (in solution) was injected into the columns and a distribution curve (relative concentration of species versus elution volume) was generated. Based on the tacit assumption of equivalence between GPC response for polystyrene and polymer X, the calibration curve was used to convert the elution volume scale (abscissa) for the distribution curve to a molecular weight scale. This latter scale displays irregular divisions which are solely determined by the shape of the calibration curve. An example of such molecular weight distribution curves is given by the UCC prepolymer (No. 10615-67/RV = 0.525) and polymer (No. 10615-112/RV = 1.50; No. 10615-98/RV = 5.12) data[3] shown in Figure 3. Note that the polydispersity or broadening of the molecular weight curve increases with increasing peak maximum molecular weight.

The molecular weight averages shown in Table 5 were calculated by employing standard methods[18], and no corrections were made for factors such as peak broadening.

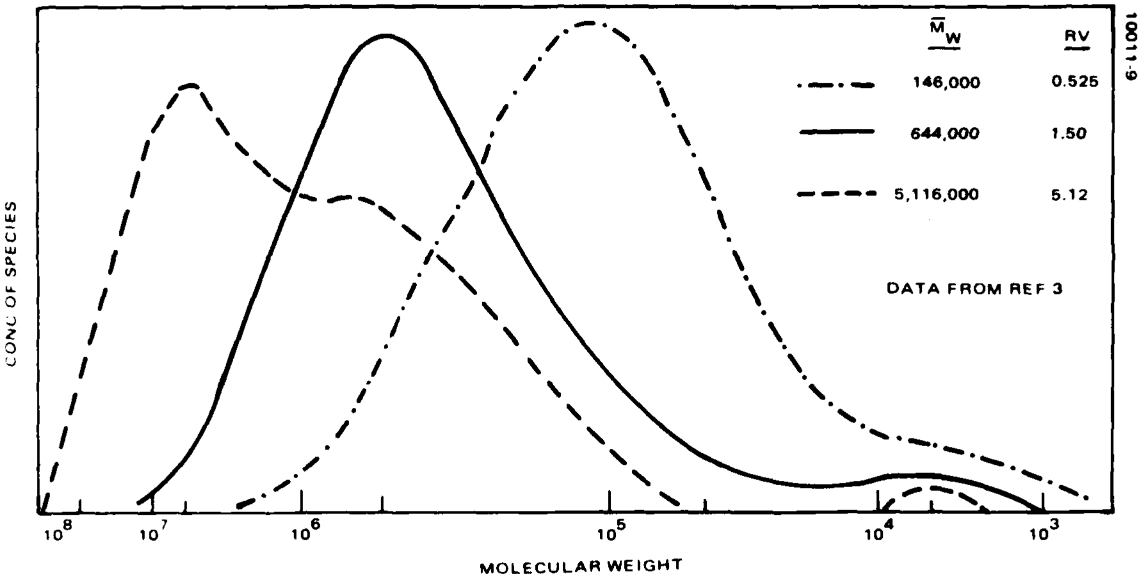


FIGURE 3. MOLECULAR WEIGHT DISTRIBUTIONS IN m-CARBORANE-SILOXANE POLYMERS OBTAINED BY GEL PERMEATION CHROMATOGRAPY (UCC DATA)

TABLE 5

COMPARATIVE REDUCED VISCOSITY AND GEL PERMEATION CHROMATOGRAPHY DATA

Specimen	RV, dl/g (25°C)	$\overline{M}_W \times 10^{-5}$	$\overline{M}_N \times 10^{-5}$	$\overline{M}_W/\overline{M}_N$	GPC Analysis[a]
PREPOLYMER					
Hughes 1392-27C	0.11	0.12	0.078	1.5	U. of MA
UCC 10615-128	0.17	0.277	0.146	1.9	U. of MA
UCC 10615-126	0.33	0.733	0.303	2.4	U. of MA
Hughes 1392-5	0.48	0.781	0.422	1.9	U. of MA
UCC 10615-67	0.525	1.46	0.513	2.8	UCC
UCC 10615-69	0.53	1.61	0.456	3.5	UCC
Hughes 1392-11	0.76	1.01	0.516	2.0	U. of MA
Hughes 1393-58-9[b]	0.88				U. of MA
UCC 11233-71	0.97	3.05	1.74	1.8	U. of MA
UCC 11233-71	0.97	3.58	0.58	6.2	Hughes
UCC 10615-68	0.98	3.79	0.729	5.2	UCC
POLYMER					
Hughes 1392-23B	1.43	3.55	1.72	2.1	U. of MA
UCC 10615-112	1.50	6.44	3.95	16.3	UCC
UCC 10615-75	2.55	16.80	–	–	UCC
UCC 11592-1-2	2.60	11.6	1.23	9.5	U. of MA
UCC 11592-1-2	2.60	10.2	2.96	3.4	Hughes
UCC 11233-72	3.23	8.97	1.79	5.0	U. of MA
UCC 11233-72	3.23	5.97	2.01	3.0	Hughes
UCC 11233-72	3.23	6.56	0.57	11.5	UCC
UCC 10615-80	3.64	22.3	–	–	UCC
UCC 10615-98	5.12	51.2	–	–	UCC

NOTES:

a: Hughes Aircraft Company – Malibu Research Laboratory
University of Massachusetts – Chemical Engineering Department/Goessmann Laboratory
Union Carbide Corporation (UCC) – Chemical and Plastics Laboratory (Bound Brook, New Jersey)

b: Advancement attempt using prepolymer 1392-27C.

b. Solution Viscometry

Dilute solution viscometry is typically performed by comparing the efflux time of a dilute polymer solution flowing through a capillary viscometer with the efflux time for a corresponding flow of the pure solvent, the temperature being the same in both cases. Of the several designated solution viscosity terms, reduced viscosity (RV) is defined as follows:

$$\eta_{red} \quad RV = \eta_{sp}/c = \frac{\eta(\text{solution}) - \eta(\text{solvent})}{\eta(\text{solvent})\, c} = \frac{t(\text{solution}) - t(\text{solvent})}{t\ (\text{solvent})\, c}$$

where:

η_{red} = reduced viscosity, dl/g

c = polymer concentration in solution, g/dl

t = efflux time, sec

For the work reported herein, $c = 0.2$ g solute per dl of solution, the solution and solvent temperatures were both 25°C, and the solvent was chloroform in all cases. By extrapolating η_{sp}/c vs c to zero concentration the effects of polymer-polymer interactions are removed, and the intrinsic viscosity $[\eta]$ is obtained as follows:

$$\lim_{c \to 0} (\eta_{sp}/c) = [\eta] \qquad (2)$$

Huggins[19] proposed the following relationship for the concentration dependence of the reduced viscosity of dilute polymer solutions:

$$RV = \eta_{sp}/c = [\eta] + k'\,[\eta]^2\, c \qquad (3)$$

Thus, when comparing RV values of very dilute polymer solutions of the same concentration in the same solvent, RV ≈ $[\eta]$.

c. Correlation Between RV and Molecular Weight

For monodisperse polymer fractions, an empirical relationship between intrinsic viscosity and molecular weight is given by Mark and Houwink modification of the Staudinger equation[20] as follows:

$$[\eta]_i = K\, M_i^{a} \qquad (4)$$

For polydisperse specimens, equation (4) is modified as follows:

$$[\eta] = K \, \overline{M}_v^{\alpha} \qquad (5)$$

where:

$\overline{M}_v$ = viscosity average molecular weight

α = constant with a value of $0.5 < a < 1.0$

K = constant (Note: Based on assumption[21] that K is independent of $\overline{M}_v$ and depends only on polymer-solvent interactions and somewhat on concentration).

Flory[22] states that $\overline{M}_v$ "depends on the nature of the intrinsic viscosity - molecular weight relationship in each particular case, as represented by the exponent α of the empirical relationships (4) and (5) above." For polymers having the "most probable" distribution, Flory presents the following relationship between several molecular weight averages:

$$\overline{M}_w : \overline{M}_v : \overline{M}_N = 2 : [(1 + \alpha) \; \Gamma(1 + \alpha)]^{1/\alpha} : 1 \qquad (6)$$

where:

$\Gamma(1 + a)$ = gamma function of $(1 + \alpha)$.

Hedaya et al.[23] reported the value of $\alpha = 0.72$ for these polymers. Based on this α value, $\Gamma(1 + \alpha)$ is found[24] to be 0.91258. Using this value of the gamma function, the term $[(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha}$ is computed to be equal to 1.87 and, thus, yields the following relationship:

$$\overline{M}_w : \overline{M}_v : \overline{M}_N = 2 : 1.87 : 1 \qquad (7)$$

Additionally Flory concludes that "$\overline{M}_v$ will always be considerably closer to $\overline{M}_w$ than to $\overline{M}_N$ for any distribution likely to be encountered in a high polymer." It is acknowledged that as polydispersity moves away from the most probable case, the situation becomes more complex.

In the present case then it is reasonable to assume the RV approaches $[\eta]$ in value and $\overline{M}_v$ approaches $\overline{M}_w$ in value. Therefore, the following approximation should be valid for the dilute polymer solutions:

$$RV \propto K \, \overline{M}_w^{\alpha} \qquad (8)$$

This approximation indicates that in a polydisperse system, RV is a power function of $\overline{M}_W$, and log (RV) vs log ($\overline{M}_W$) should plot a straight line with slope equal to α. Figure 4 does indeed display this relationship between log $\overline{M}_W$ and log (RV) for the UCC materials analyzed at UCC. Hughes materials analyzed at the University of Massachusetts seem to fall on a line (not drawn) offset from the UCC materials line. It will be noted that in all three GPC locations, tetrahydrofuran was the solvent used. It has been shown in the literature that changes in operational variables such as sample size[25] and concentration[26] can effect GPC results Some changes in this regard have been made from run to run during the course of this work (i.e., at University of Massachusetts and Hughes). These changes have been minor and are not believed responsible for the large deviation observed. Additional speculation regarding the discrepancy between Hughes and UCC materials data is as follows:

- Varying amount of basic impurities in the tetrahydrofuran solvent may have caused varying molecular weight degradation in the measured polymer specimens, or degradation caused by shear may have occurred in the polymers during GPC analysis.

- GPC analyses are accurate, and the variation in data is in some way related to the polymerization process and the varying distribution in prepolymer/polymer molecular weight.

- Assumptions made during the analysis of the molecular weight data by the two research groups (Hughes and Union Carbide) may not have been consistent.

Although no theoretical basis exists for correlating $\overline{M}_N$ with RV, the available data for prepolymers were assembled arbitrarily from Table 5 and plotted in Figure 5. As noted, a line was drawn through points of low polydispersity. This has been used as a scaling factor for estimating silanol contents using the end group analysis discussed earlier and appears to be valid as long as the RV values remain below approximately 1.0. Above this point the polymer seems to display a distinct low molecular weight tail in the GPC trace as shown in Figure 3, and accurate calculation of meaningful $\overline{M}_N$ data becomes more difficult.

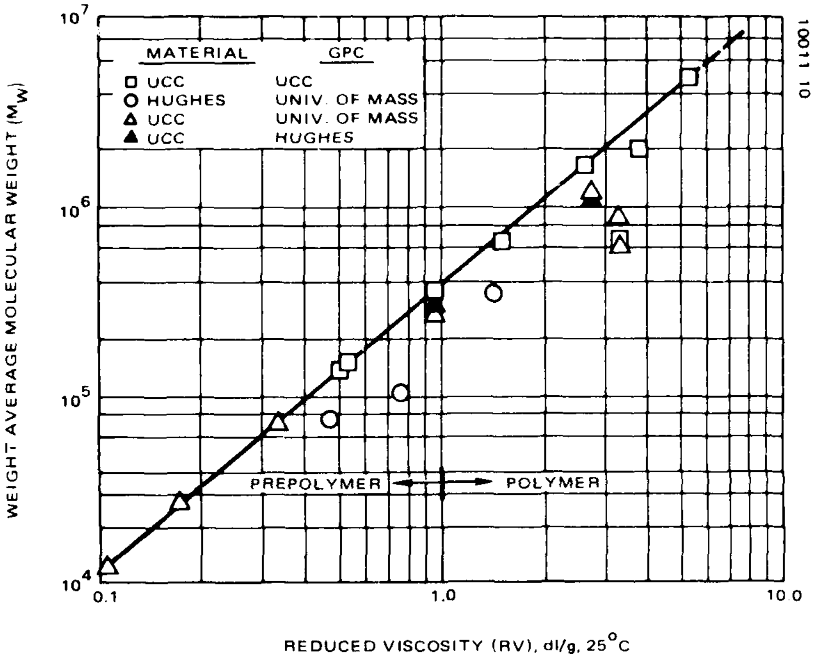


FIGURE 4. CORRELATION OF WEIGHT AVERAGE MOLECULAR WEIGHT ($\overline{M}_W$) WITH REDUCED VISCOSITY (RV)

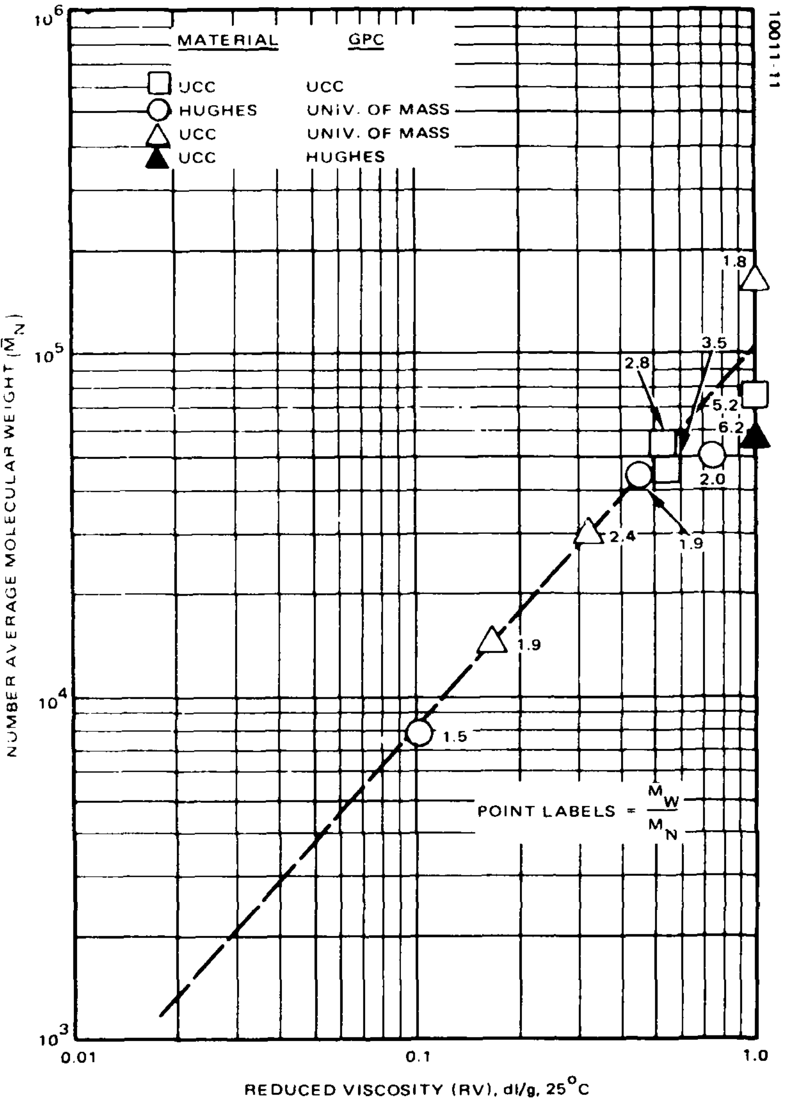


FIGURE 5. ROUGH GRAPHICAL ESTIMATE OF RELATIONSHIP BETWEEN NUMBER AVERAGE MOLECULAR WEIGHT ($\overline{M}_N$) AND RV FOR PREPOLYMERS

SECTION III

ADHESIVE FORMULATION

Adhesive formulation efforts were quite limited due to the difficulties encountered in the synthesis of materials. Nevertheless, some experiments were undertaken and plans were made for future work. The discussion of these topics will be organized into three parts. The first part will deal with work which has been done in previous studies.[1] The second part will deal with formulation attempts and plans, and the third part will discuss characterization of formulated materials.

1. PREVIOUS WORK

The problem of thermally induced embrittlement as a result of crosslinking in the range of 500-600°C confined material consideration to a thermoplastic species, namely, polycarborane-siloxane. Resorting to a thermoplastic species, however, introduced the problem of striking a balance between a) 600°C viscosity sufficiently high to minimize creep and plastic flow and b) processing viscosity (at approximately 150°C maximum) sufficiently low to permit adhesive bonding at moderate pressure and dwell (approximately 15 psi and 24 hours). In other words, a compromise was required to assure acceptable dimensional stability at 600°C and acceptable processibility at lower temperature, both factors being considered in the context of the dominant consideration of acceptable resistance to high temperature embrittlement. Thus there was a need to restrict consideration to a very viscous thermoplastic material. At this point, the concept of a mutually compatible blend of low and high molecular weight polymers became attractive. The low molecular weight constituents would serve to inhibit high temperature embrittlement while the high molecular weight constituents would introduce the necessary viscosity to minimize creep or plastic flow at service temperature. Ultrahigh molecular weight polymers were considered most advantageous because they would permit use of the maximum contents of low molecular weight species without loss of requisite viscoelastic properties at processing (150°C maximum) and service (50°C maximum) temperatures. This results from the strong dependency of viscosity, η, on molecular weight as shown in equation 9.

$$\eta = K\,(\overline{M}_w)^{3.4} \qquad (9)$$

Experimentally, several blended and nonblended systems were characterized and one blend system in particular was found to be attractive and was selected for thermal cycling and adhesive testing. The results of this work were encouraging showing good retention of properties after cycling and predominantly cohesive failure in peel testing.

2. FORMULATION ATTEMPTS

In the previous studies, samples were prepared by slow solvent casting from methylene chloride onto a teflon substrate. This allowed the production of reasonably thin and uniform films. Characterization efforts, in particular thermal analysis, indicated that compatible blends were produced.

Casting techniques using methylene chloride as the solvent were also explored in this program. The polymers blended were UCC 10615-128, an all dimethyl carborane-siloxane material with $\overline{M}_w = 2.8 \times 10^4$, and UCC 10615-126, a modified carborane siloxane containing some methyl phenyl species and having an $\overline{M}_w = 7.3 \times 10^4$. These materials were blended in a 50:50 ratio by weight and cast onto a teflon surface. Solvent evaporation rate was varied from rapid (<1 hr) to slow (>24 hrs). In all cases the films produced were of poor quality. It is suspected that this was due to the fact that both materials were of relatively low molecular weight (for polycarborane siloxane materials) and each had a hard waxlike integrity in the nonblended state. In the previous work, the weight average molecular weights of the blended species were quite a bit higher, namely, 5.0×10^4 and $\gg 1.0 \times 10^6$.

It was conceived that since the material blends, when properly formulated, would be quite viscous, it probably would be possible to form films from powdered materials in the melt state in a heated press. If successful this would eliminate many of the problems typically associated with solvent casting of blended materials. Since it is likely that only small amounts of material would be synthesized, melt blending and film extrusion is not a possibility.

An initial attempt at forming a blended powder using the same mix ratio and materials previously discussed was conducted by first dissolving the materials in methylene chloride. The solution was then introduced into a blender filled with boiling water. The methylene chloride (b.p. 40°C) flashed off leaving the polymer which is insoluble in water. Some difficulty was encountered, in that during the process the polymer blend is raised above its T_g and as a consequence forms a film on the container and also precipitates as tacky waxlike particles, rather than the desired flocullated precipitate. This makes the process of sample recovery tedious, but not impossible. The issue of whether this process causes molecular weight segregation (incompatibility) was not explored. Another method which was not attempted, but which is quite common, is to precipitate the blend from methylene chloride using a nonsolvent. Methanol would appear to be an excellent choice since it is used in this capacity in the work-up procedure. This technique then eliminates the need to subject the polymer blend to temperatures greater than ambient and should result in a more easily handled product. It is envisioned that the powder blends would then be molded into films of consistent thickness and homogeneity using a suitably designed mold and a standard heated press.

3. CHARACTERIZATION OF FORMULATED MATERIALS

The characterization of formulated materials should be directed initially to determine the homogeneity of the films produced. One technique to do this, which has been used in previous work, is Differential Scanning Calorimetry (DSC). Using this technique, it is possible to determine T_g as well as measure the amount and temperature of any crystallite melting. Another useful tool for observing compatibility is the Rheovibron dynamic viscoelastomer. Films can be directly analyzed in an oscillatory tensile mode. Data indicating material transitions, as well as absolute modulus values, can be obtained. In many cases, this mechanical technique is more sensitive to material transitions than thermal methods. Finally, direct observations of the films using scanning electron microscopy would also be valuable. A secondary characterization concern is the measurement and potential alteration of processing characteristics. These investigations would be best accomplished by measuring viscosity and viscoelastic response on an instrument such as the Rheometrics Mechanical Spectrometer. Experimental plans have been formulated to guide the use of all the above mentioned techniques in the adhesive characterization effort and will be used in continuing efforts with these materials.

SECTION IV

SUMMARY

The principle objectives of this work were (a) the development of a reproducible synthesis for ultrahigh molecular weight, linear m-carborane-siloxane polymers and (b) the confirmation of their usefulness as adhesives exposed to transient thermal extremes (-196 to 600°C) in vacuum.

In terms of polymer synthesis reproducibility, major progress has been made. This progress has involved the following accomplishments:

- Verification of reproducibility of monomer preparation and purification, i.e., for m-carborane-disilanol, bisureido-methylphenylsilane, and bisureidodimethylsilane.
- Verification of the reproducibility of prepolymer preparative chemistry via the titration of m-carborane-disilanol with mixed bisureidosilanes.
- Development of a silanol end group analysis employing a specially synthesized/purified ureidosilane reagent to end cap free silanol groups. Detection of end capped species is accomplished by IR spectrometry and is sensitive to silanol concentrations as low as 10^{-5} to 10^{-6} molar.
- Demonstration, by means of the silanol end group analysis, that desired high silanol content in the prepolymer is determined by prepolymer preparation parameters and is not related to subsequent prepolymer workup conditions.
- Limited demonstration that high silanol content in the prepolymer is a requirement for further molecular weight advancement.

Additional work is required in order to achieve the primary goals of the program. This work includes the following tasks which have not yet been accomplished:

- Further refinement in optimum reaction conditions for prepolymer preparation.
- Definition of process parameters for the reproducible advancement of high silanol content prepolymer to ultrahigh molecular weight polymer.

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- Definition of formulation techniques using ultrahigh molecular weight polymer to generate a thermoplastic film adhesive.
- Evaluate adhesive bond line stability (using fused silica fabric and aluminum adherends) over the thermal regime -196 to 600°C.

Inability to fully define the preparative chemistry during the eight-month experimental period allotted prevented any serious address to the tasks of adhesive formulation and evaluation.

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APPENDIX

INERT ATMOSPHERE EQUIPMENT AND MANIPULATIONS - PURIFICATION OF REACTANTS AND SOLVENTS

There are several general approaches to inert atmosphere manipulations: glove (dry) box, syringes, and special (Schlenk) glassware. All of these techniques were routinely employed for the synthesis of carborane-siloxane polymers. For example, the Dry Box is definitely the best means of handling and storing the air sensitive, solid bisureidosilanes; however, in our opinion the synthesis of monomers and polymerization experiments are best carried out on the bench using Schlenk equipment. In his book, Shriver* has presented an outstanding description of these techniques. A brief discussion of each method along with Hughes modifications and suggestions are given below.

Dry Box. The dry box used was obtained from Vacuum Atmospheres Inc., Hawthorne, CA., Model Number HE-43-2 with Dri-Train Number MO-40-1H. High, purity argon was the inert gas which was continuously cycled through a purifier which contained a moisture absorbent (molecular sieve) and an oxygen reducing agent (Ridox). The bisureidosilanes were stored and handled in this inert atmosphere environment as much as possible. Storage of the bisureidosilanes in Schlenk tubes equipped with high vacuum stopcocks and tightly secured stoppers (rubber bands) is recommended. Apiezon N should be used for all joints; silicon grease reacts with bisureidosilanes.

Syringe Techniques. Hypodermic syringes are convenient for transferring small amounts of liquid reagents and solvents, however, multiple transfers are not recommended. The alternative double-ended needle technique is especially good for medium and large quantities of very air sensitive materials, and was used routinely in our work for transferring reactants and solvents.** After completion of the operation, removal of the punctured septum and replacement with a conventional ground glass stopper is recommended. Experience indicates that septums cannot be used for extended periods when working with bisureidosilanes.

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* D. F. Shriver, The Manipulation of Air Sensitive Compounds, McGraw-Hill, 1969.

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Schlenk-type Glassware and Operations. The essential feature of Schlenk apparatus is a sidearm fitted with a high vacuum stopcock to permit evacuation and purge with inert gas. High vacuum is not necessary because the purge cycle is repeated several times. A manifold equipped with two-way stopcocks attached to a source of purified argon and vacuum was employed.

All glassware was carefully cleaned and oven dried for 12 hours at 150°C. The glassware was then removed and assembled while warm in an atmosphere of dry argon. The apparatus was then evacuated and purged a minimum of three times with purified argon. All bench manipulations were carried out in this manner.

Purification of Reactants and Solvents

Pyrrolidine (Fisher Lot Number 782420) was refluxed over potassium hydroxide pellets for 15 hours and distilled under argon, bp 87-88°C.

Argon (High Purity) was further purified by passing the gas through a 36 inch column of Drierite, a 36 inch column of Ridox (Fisher R30) oxygen scavenger, and finally a 36 inch column of Drierte.

Dichlorodimethylsilane (PCR Product Number 27220-3, Dow Corning Repackaged Lot Number 9440) was fractionally distilled through a 24 inch Vigreaux column under argon, bp 70-71°C.

Phenyl Isocyanate (Eastman Number 553, Lot Number C7C) was distilled three times at reduced pressure from P_2O_5, stored under argon, and redistilled immediately before use [bp 79-80° (39 mm)].

Diethyl Ether (Mallinckrodt 0848-1, anhydrous) was freshly distilled from dark blue sodium-benzophenone ketyl.

Hexane (Burdick and Jackson, "Distilled in Glass") was distilled from blue sodium-benzophenone ketyl.

Chlorobenzene (Fisher B254, Purified) was first distilled from P_2O_5 under argon and then redistilled from calcium hydride.

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